MALCOLM

Institute of Paper Science and Technology
Atlanta, Georgia

ANNUAL RESEARCH REVIEW

CORROSION CONTROL

SLIDE MATERIAL

March 23, 1995

INSTITUTE OF PAPER SCIENCE AND TECHNOLOGY
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- to sustain an international position of leadership in dynamic scientific research which is participated in by both students and faculty and which is focused on areas of significance to the pulp and paper industry; and

- to contribute to the economic and technical well-being of the nation through innovative educational, informational, and technical services.

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ANNUAL PROGRAM REVIEW

CORROSION CONTROL

SLIDE MATERIAL

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Corrosion Control

Annual Technical Review

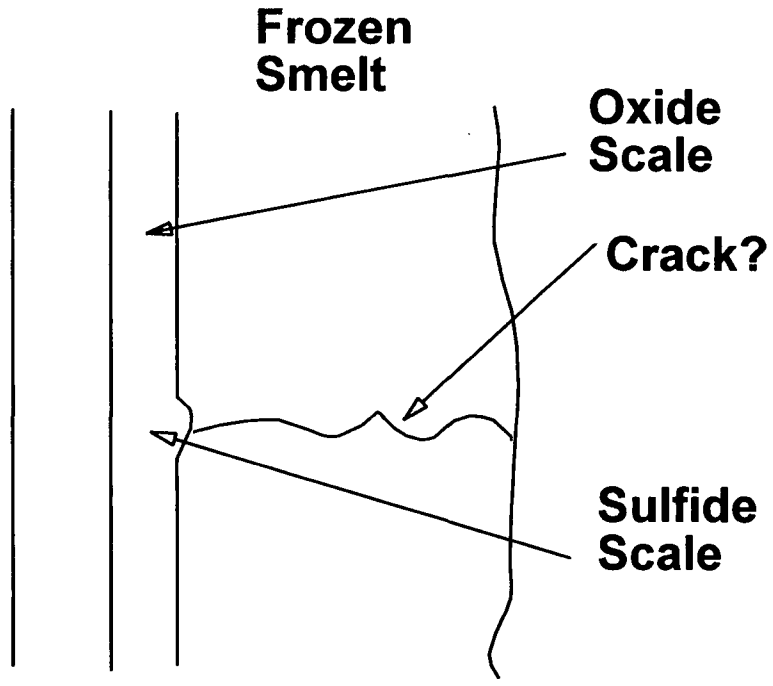
Dues-Funded Research

- F018- Recovery Boiler Corrosion
- F019- Corrosion Control in Closed-Cycle Mills

Organization of Recovery Boiler Corrosion Project

Dues-Funded (F018)	*Additional Funding Leverage*
Task 1. Gas Phase Reactions Determine Suitable C,O,S Potentials	**AF&PA Phases C&D**
Task 2. Local Measurements Develop Sensor for O and S Beneath Frozen Smelt	**DOE/AF&PA Corrosivity Monitoring**
Task 3. Long-term Kinetics Extrapolation of Lab Tests to Predict Service Performance	
Task 4. Port Corrosion Determine Mechanism to Develop Efficient Mitigation Strategy	**Ph.D. Student Estes** **ORNL/DOE Composite Tube Cracking**

Gas Phase Reactions

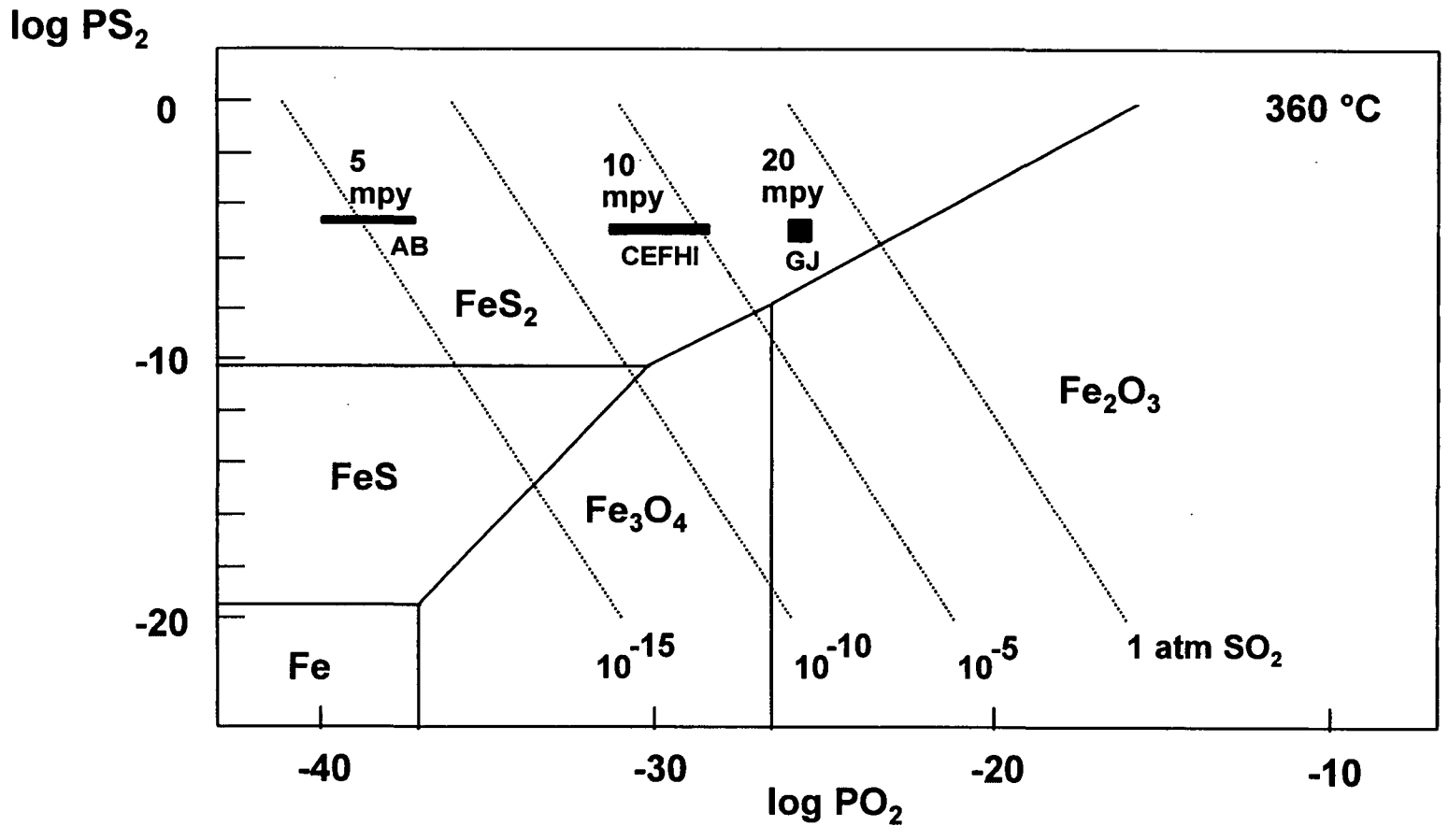


Furnace
Gas
H_2S, CO, CO_2, H_2O

Previous Results

- At Constant Ps_2, Rate Increases as Gas Approaches Oxide/Sulfide Boundary
- Cycling Across Oxide/Sulfide Boundary Causes Rapid Increase in Corrosion

Fe-S-O Phase Stability Diagram



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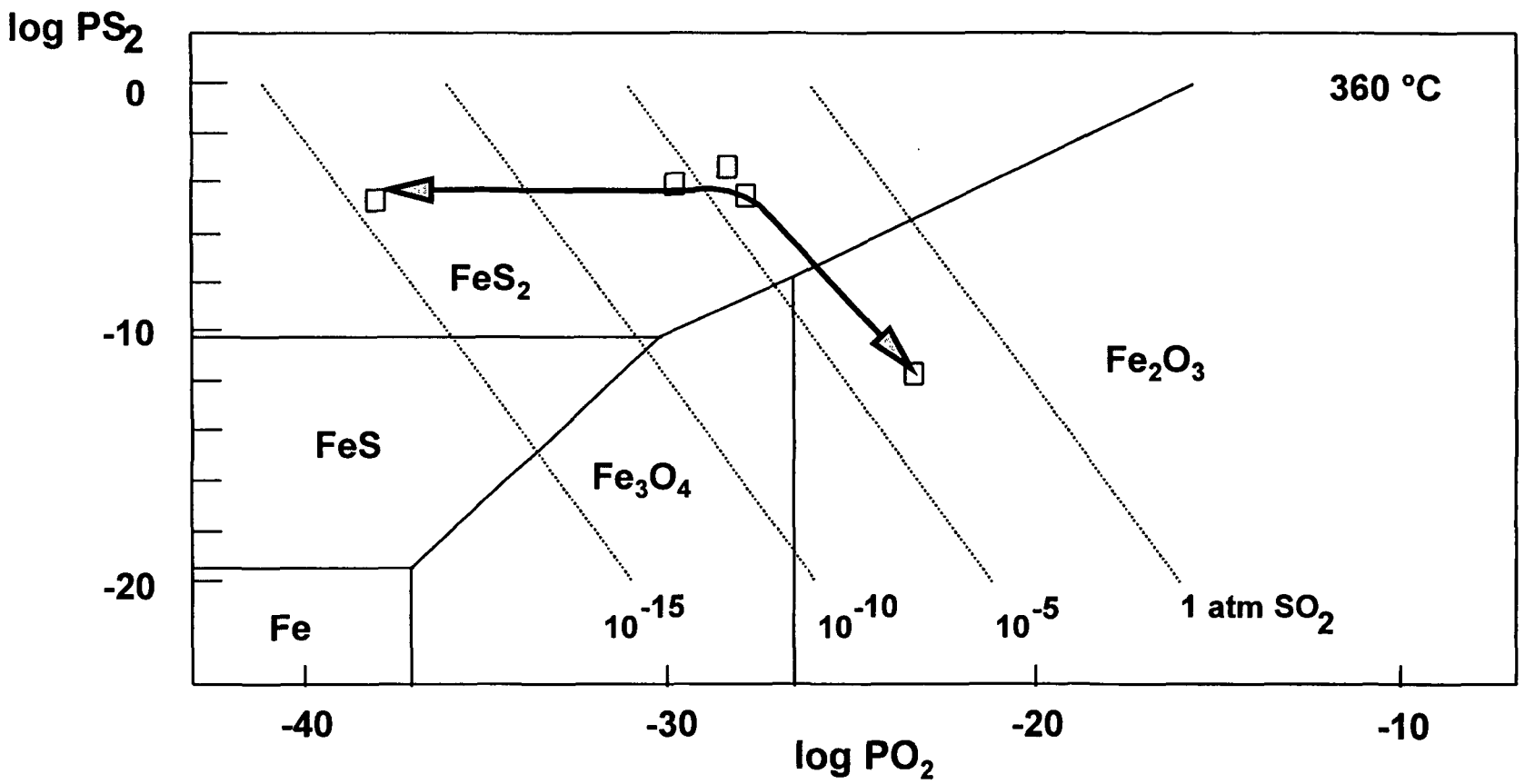
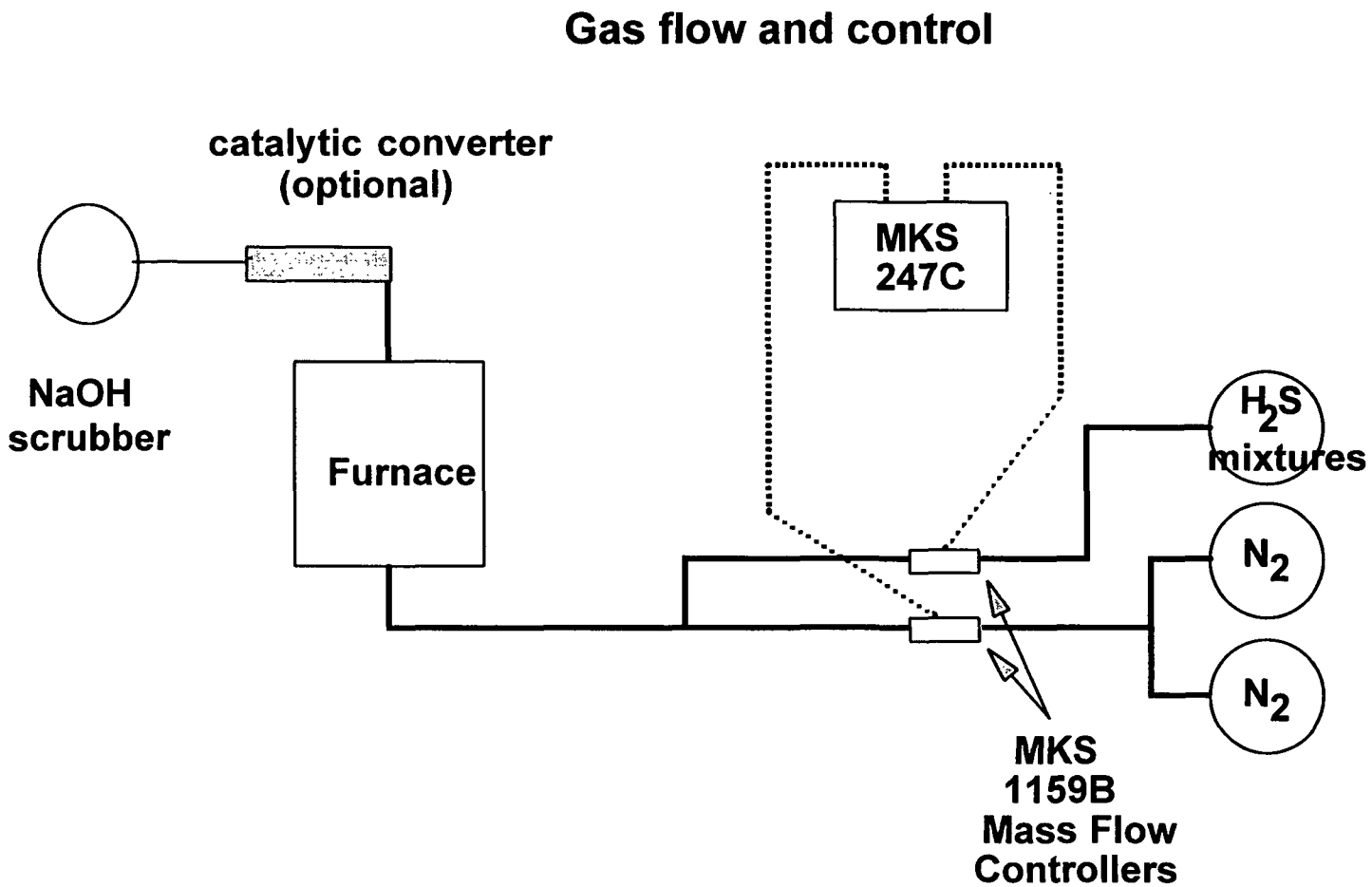
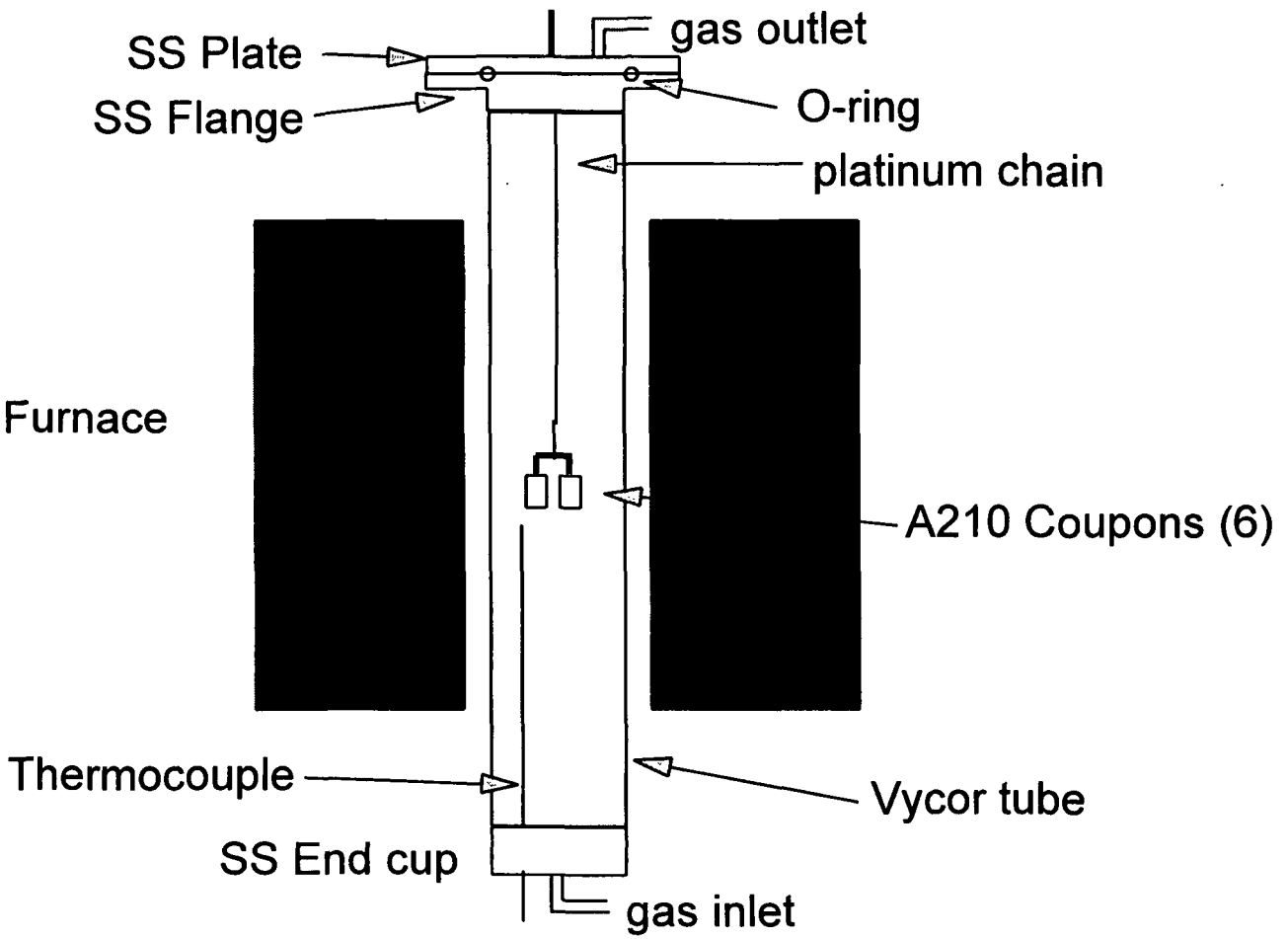


Furnace Plumbing



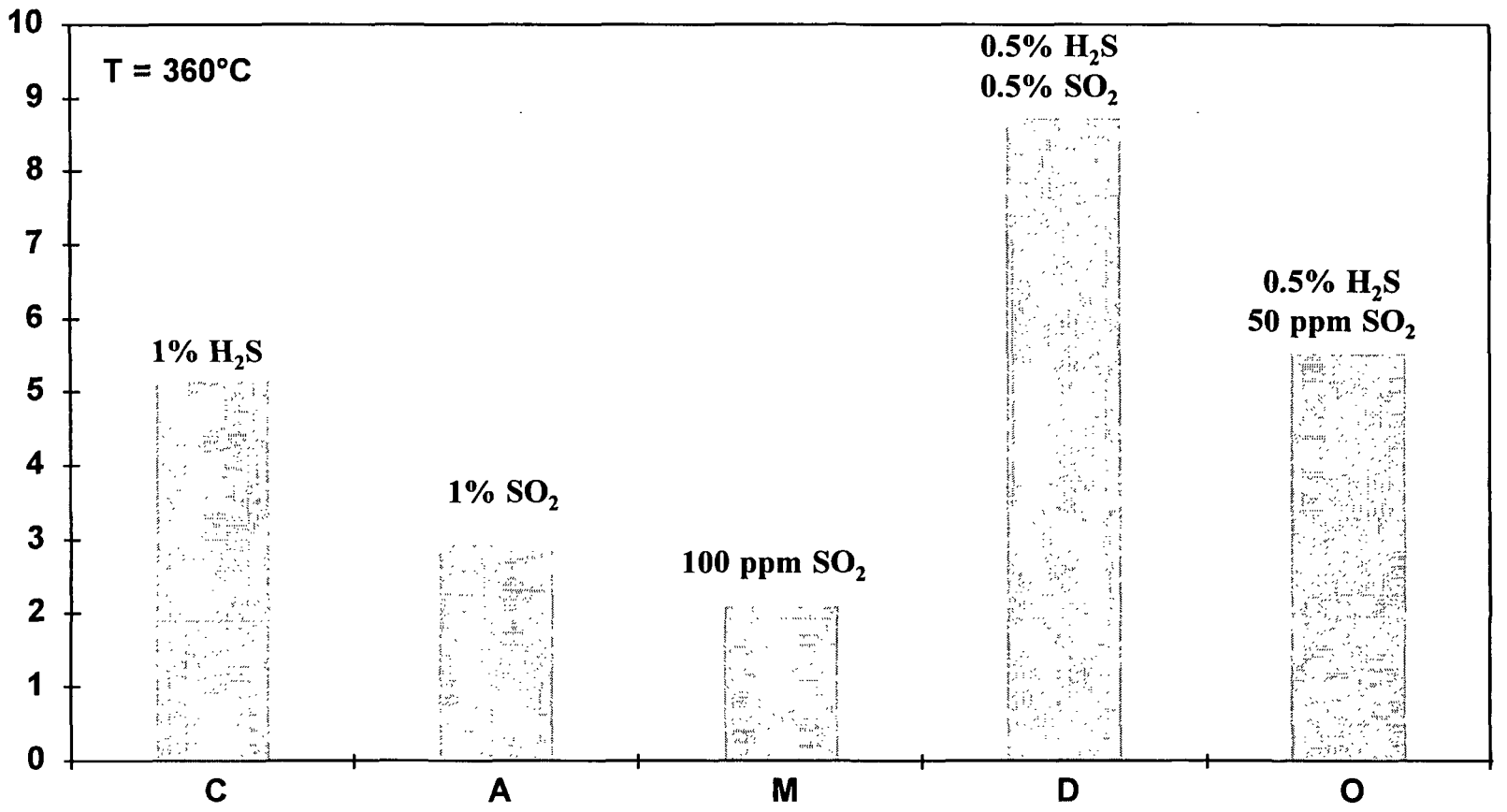
Furnace Details



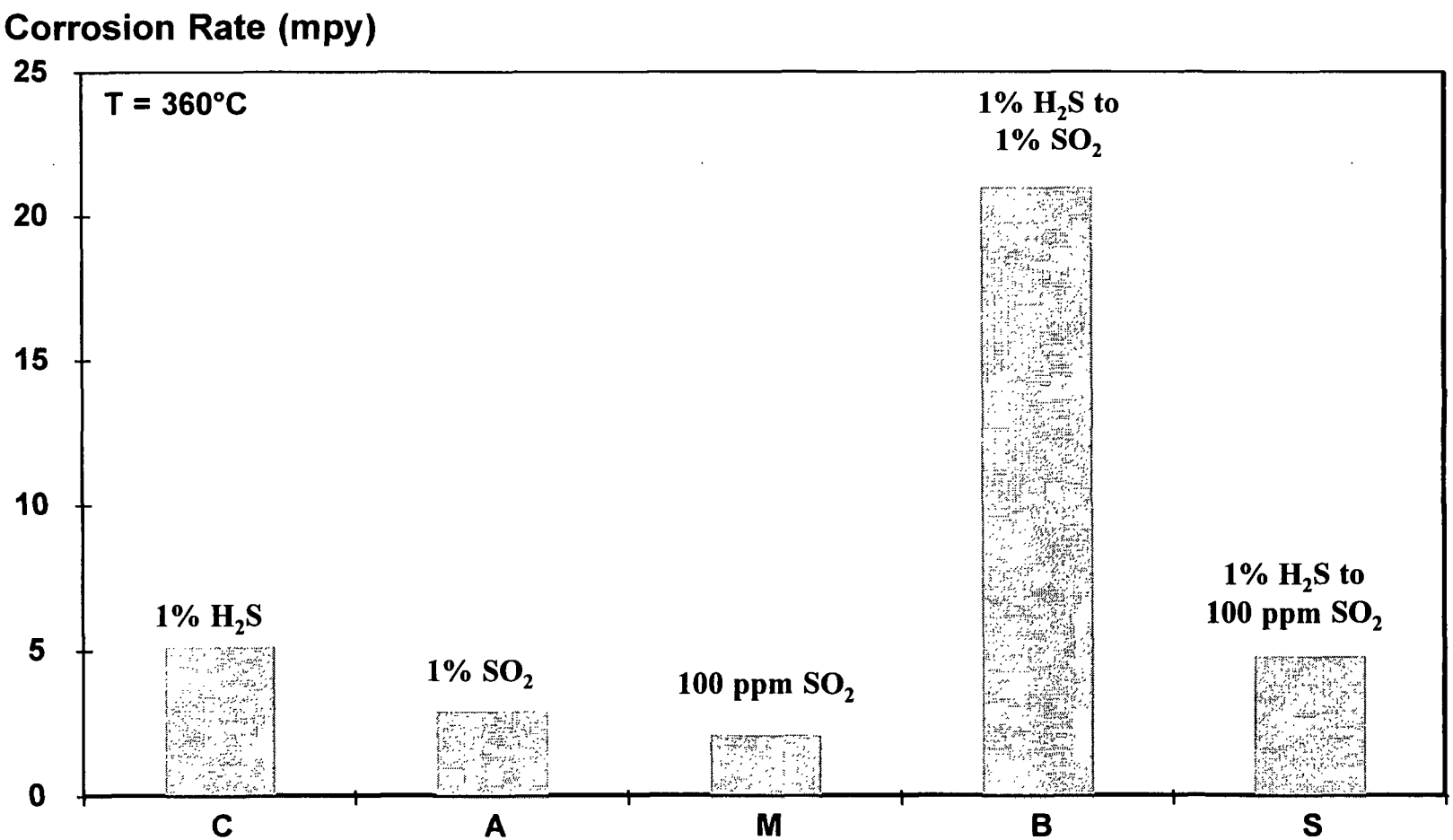
Cyclic Tests

- Will Lower SO_2 Contents Give Similar Acceleration in Corrosion Rate?
- Decrease from 1% to 100 ppm
- Thermodynamic Calculations Show This is Reasonable Range for Black Liquor Combustion

H_2S/SO_2 Static Tests



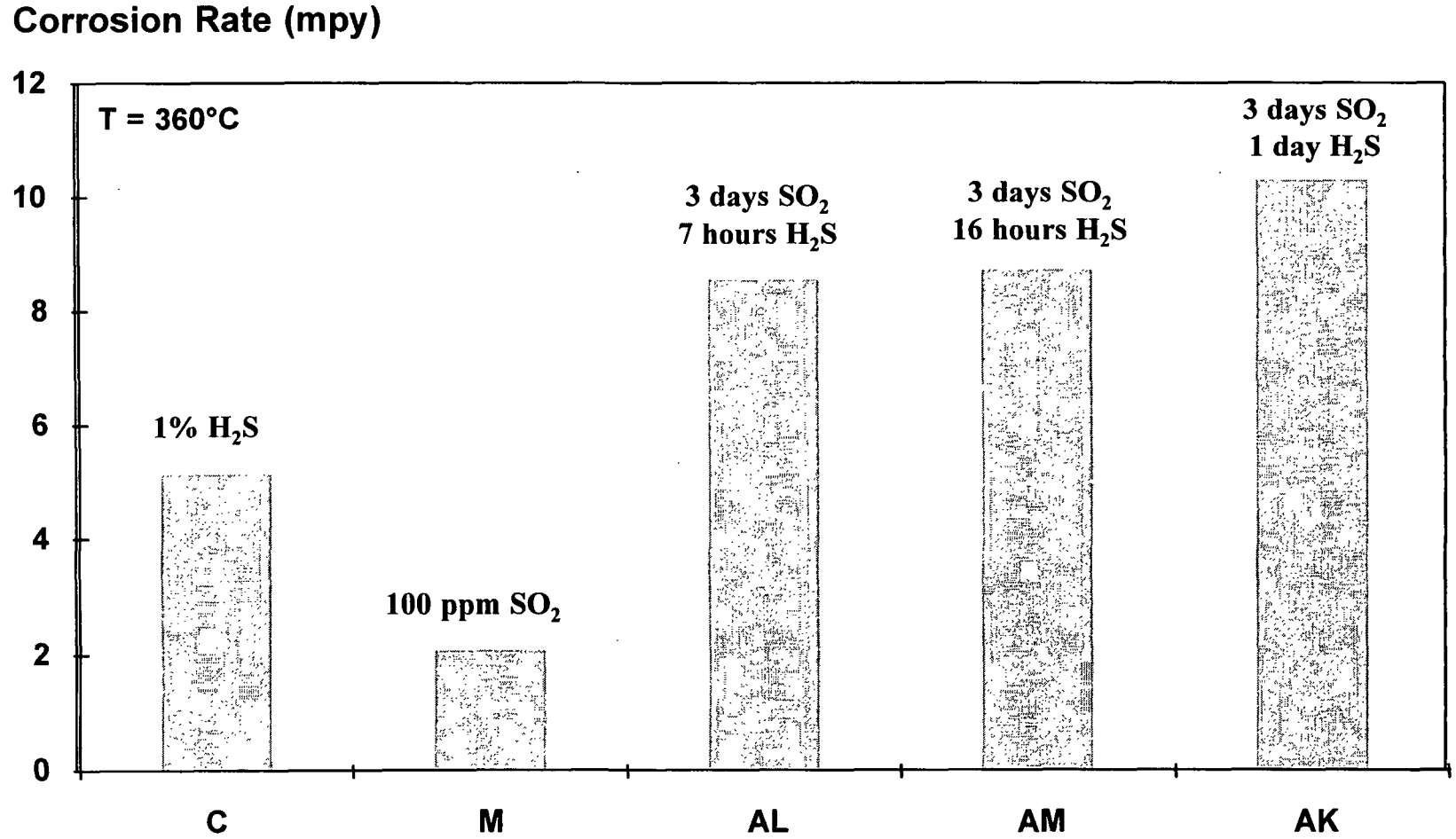
H_2S/SO_2 Cyclic Tests



Pre-oxidation Tests

- Changing From Oxide to Sulfide and Back Causes Rapid Corrosion
- How Fast is the Scale Converted?
- Does the Time of Stability in Each Phase Field Play a Role?
- Pre-oxidized for 3 days in SO_2, then Changed to H_2S for Sulfidation Run for Various Times

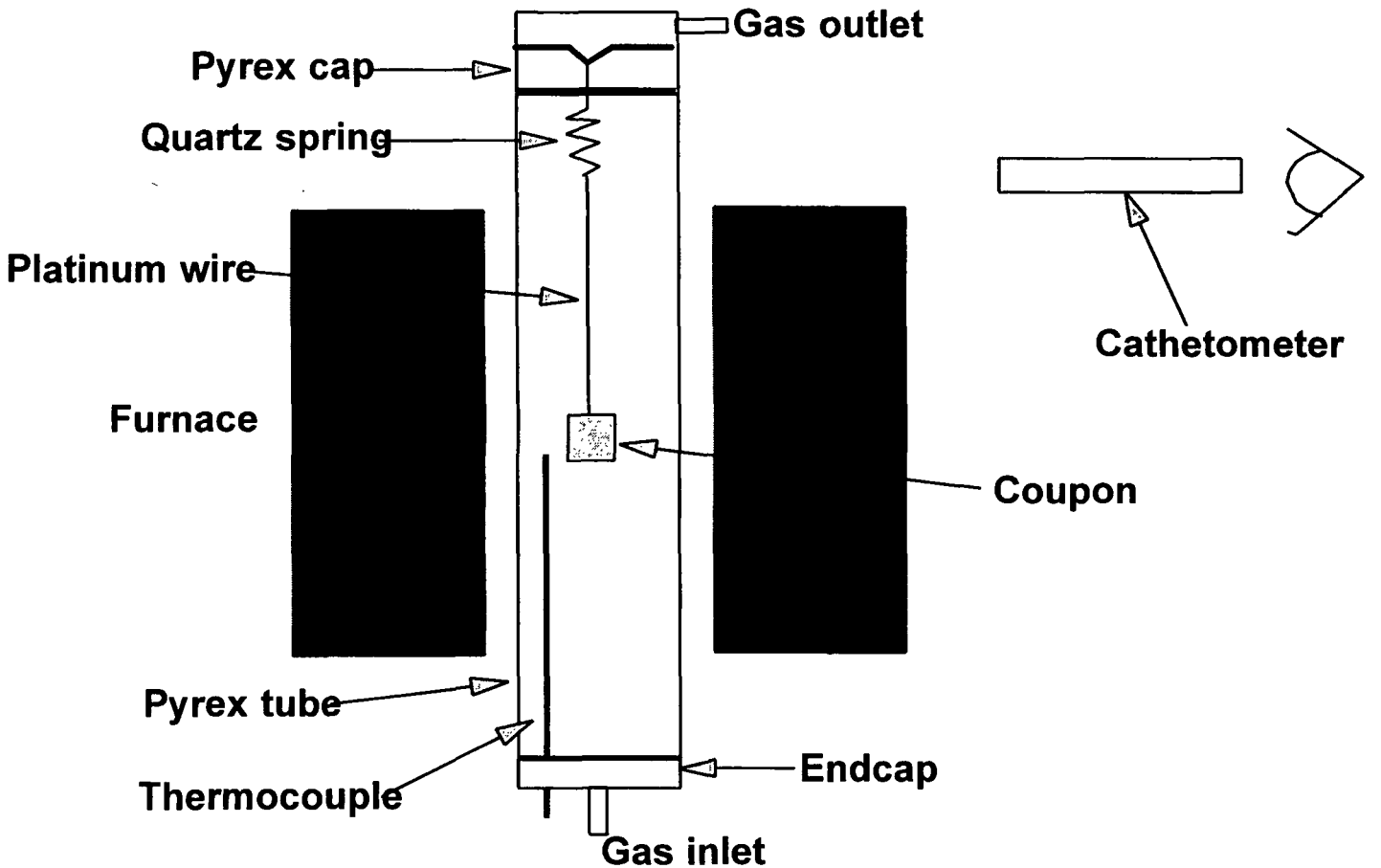
H_2S/SO_2 Pre-oxidation Tests



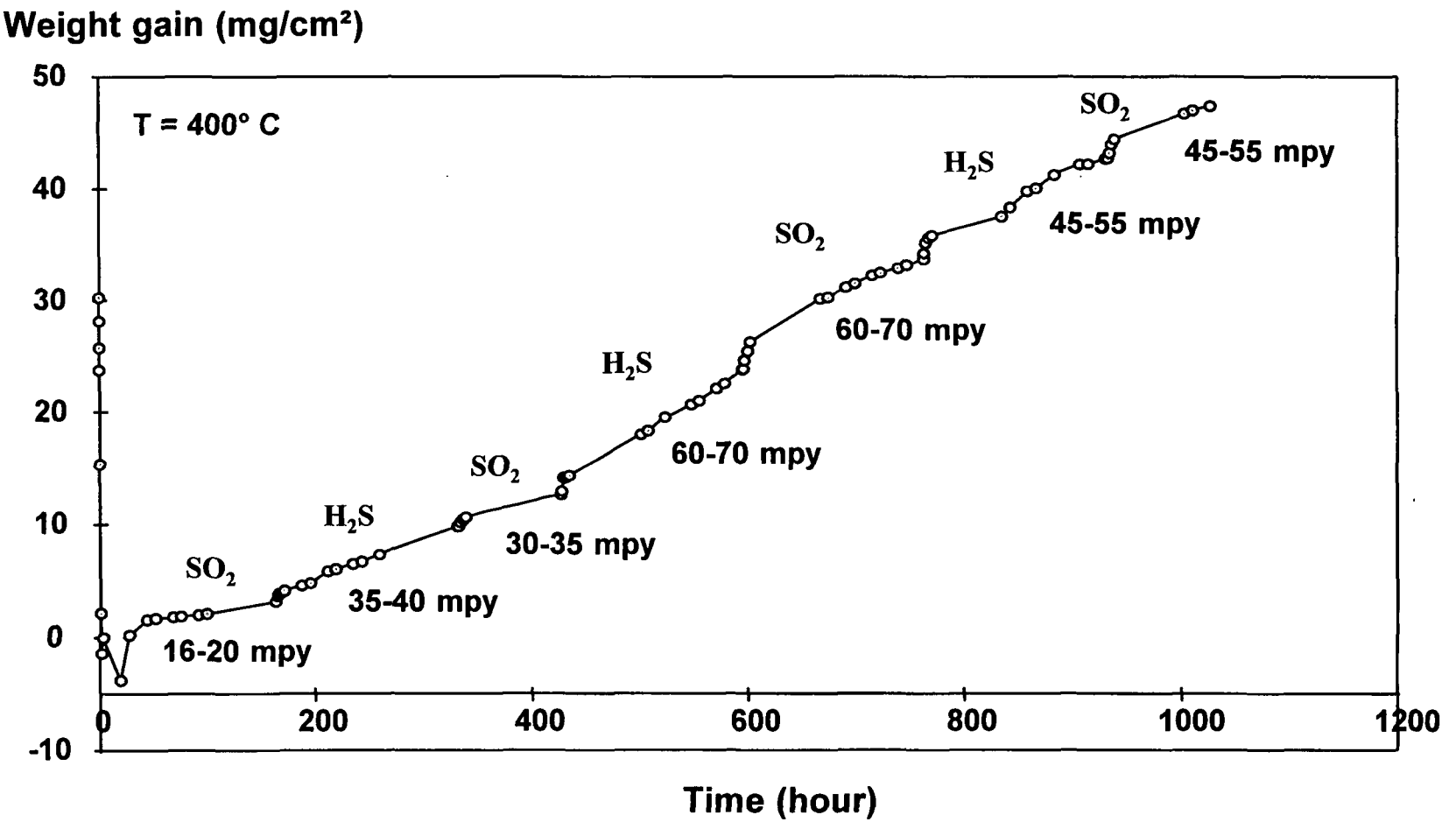
Instantaneous Rates for Alternating Oxidation/Sulfidation

- Have Average Rate Data for Acceleration of Corrosion
- How do Changes Occur?
- Is the Rate a Strong Function of Time as the Environment Changes?
- Used Thermobalance to Record Sample Weight as the Environment Was Cycled

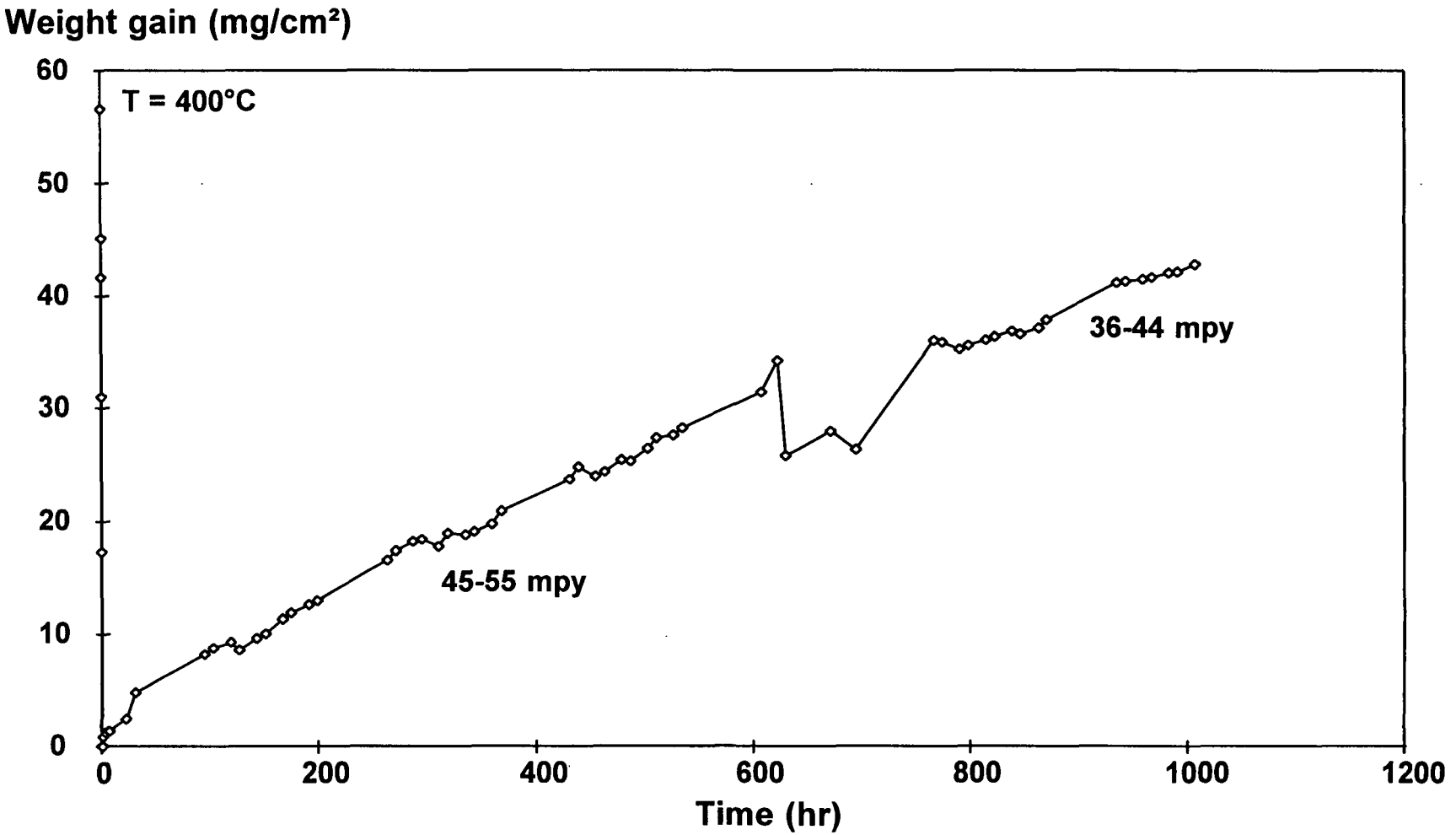
Quartz Spring Balance



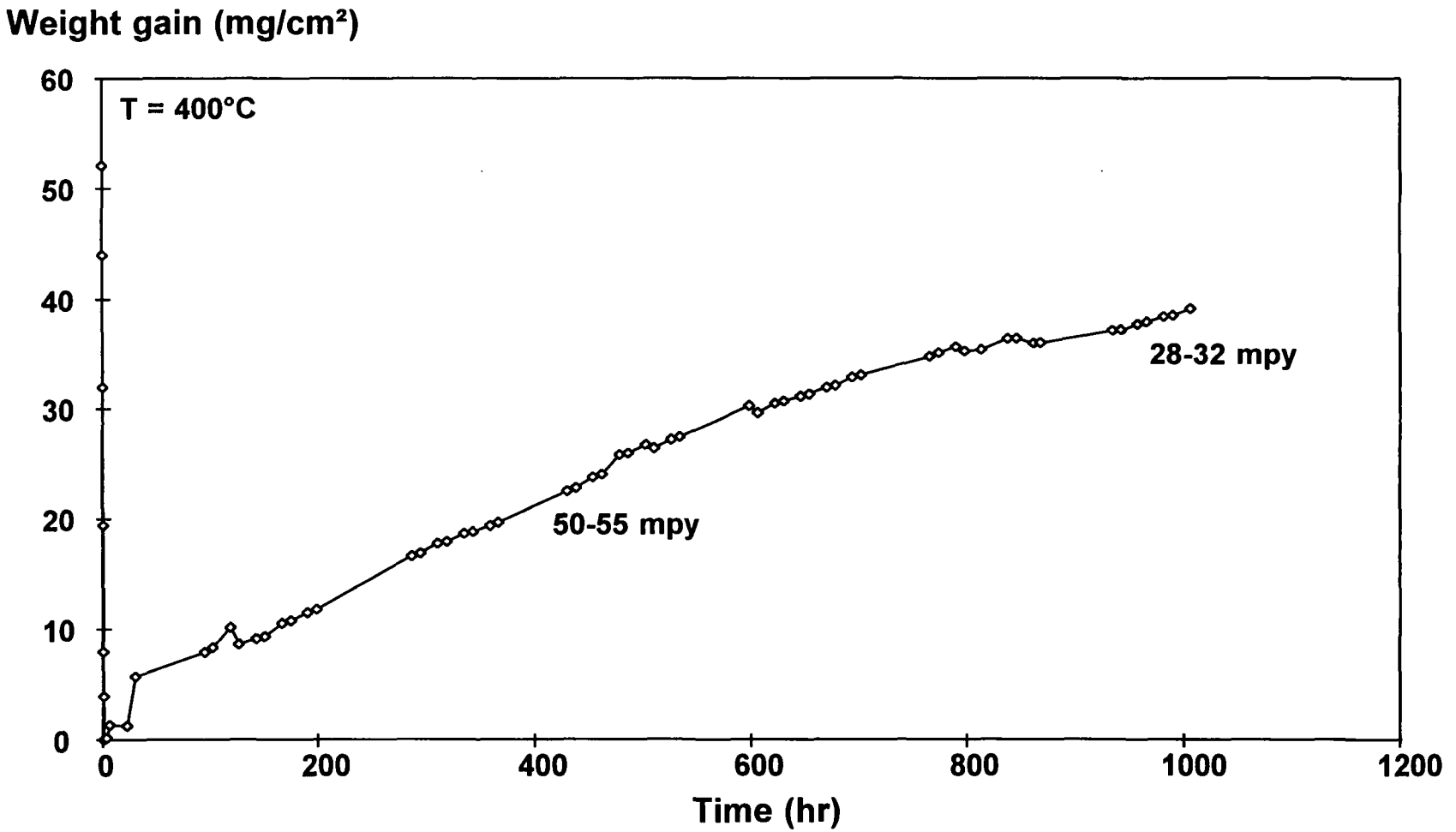
Carbon Steel Coupons in Alternating 1% SO_2 and 1% H_2S Environment



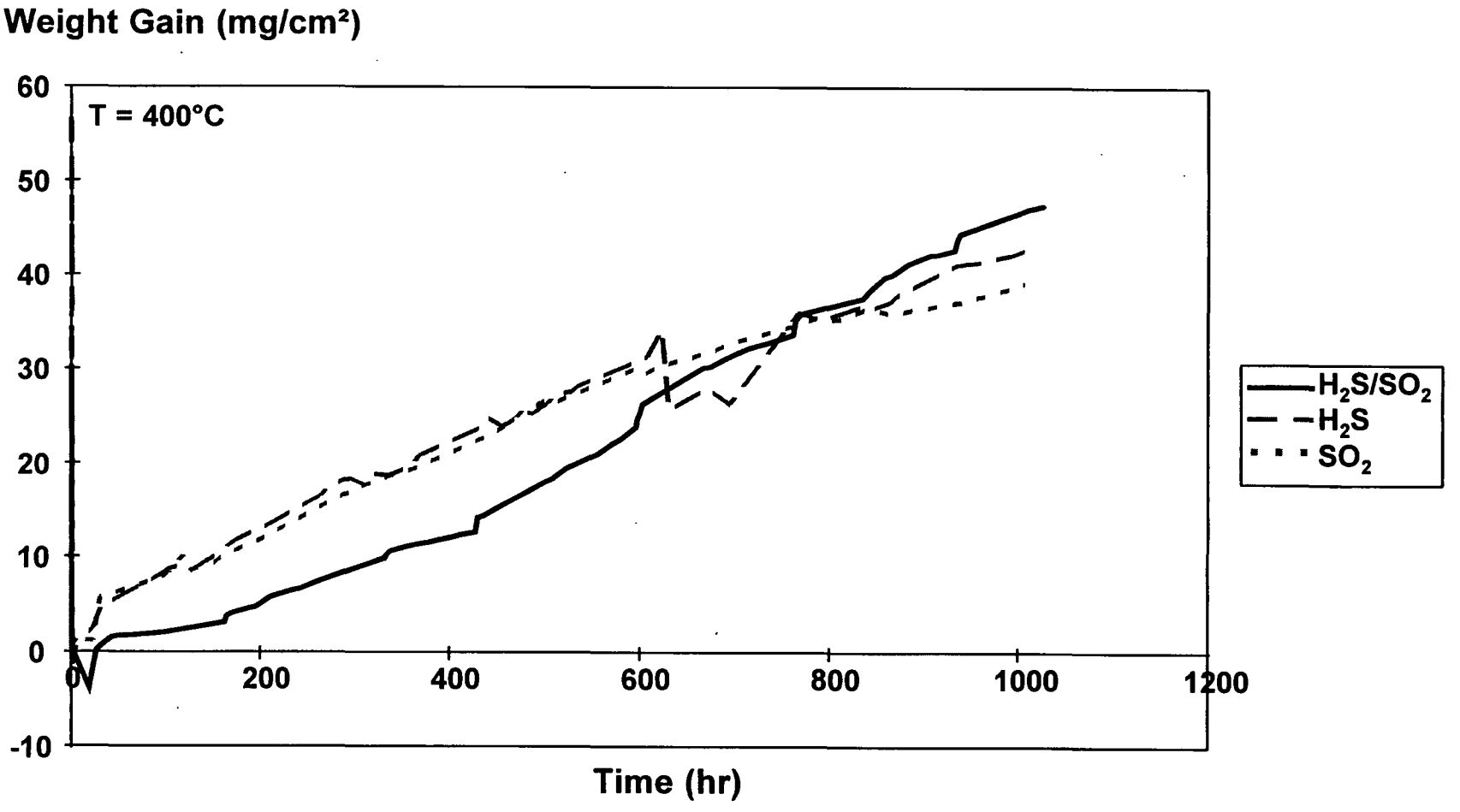
Carbon Steel Coupon in 1% H_2S Environment



Carbon Steel Coupon in 1% SO_2 Environment



Comparison of Cyclic and Baseline Tests for Carbon Steel Coupons



Port Corrosion

- Being Conducted by Ph.D. Candidate Matt Estes
- Follows Preliminary Corrosion Experiments and Model Development

Mechanism for Corrosion of Composite Tubes at Ports

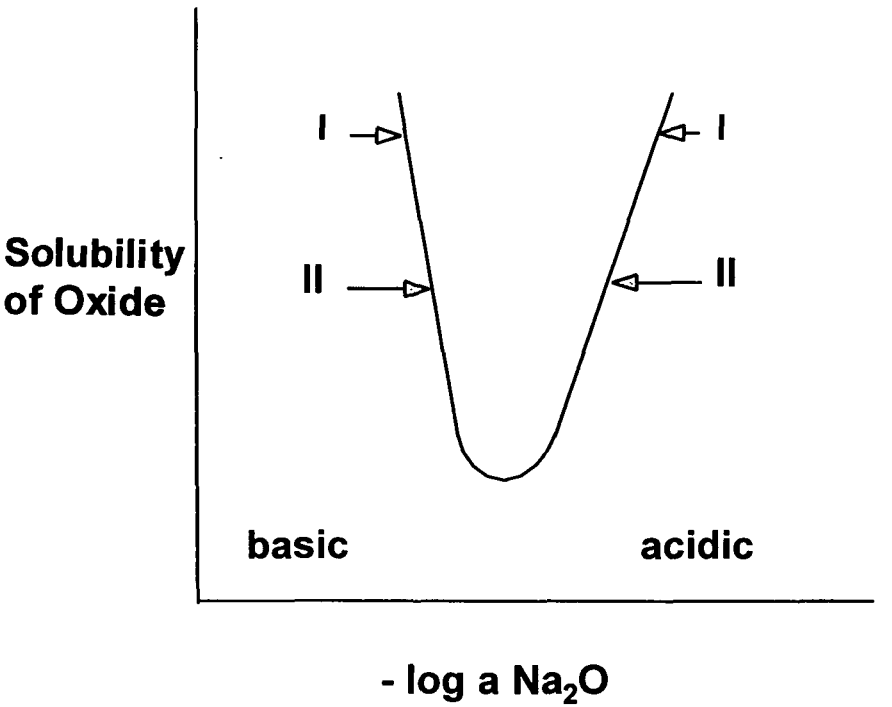
- Hot Corrosion Mechanism (molten salts)
- Salt is Hydroxide Based (field probes)
- Other Components Can Alter Melting Point
- Same Mechanism Operative in Gas Turbines and Molten Carbonate Fuel Cells

Fluxing of Corrosion Products is the Key

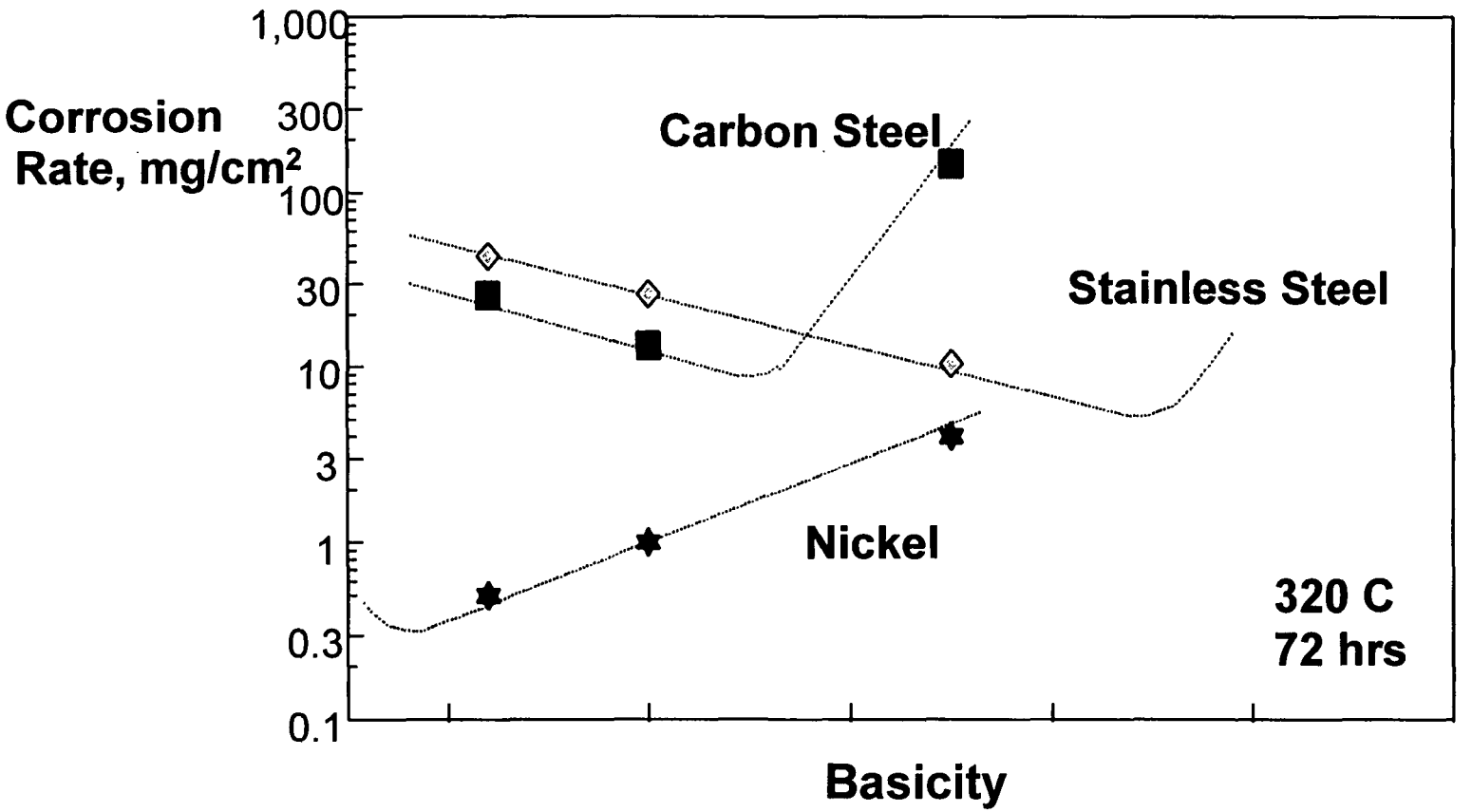
- Gradient in Oxide Solubility Across Salt Film Must be Negative for Sustained Hot Corrosion
- Solubility Decreases with Distance from Alloy Surface

Conditions for Hot Corrosion

- I: Oxide/Salt Interface
- II: Salt/ Gas Interface
- Hot Corrosion is Function of Basicity and Type of Oxide Dissolution



Corrosion Rate vs. Basicity



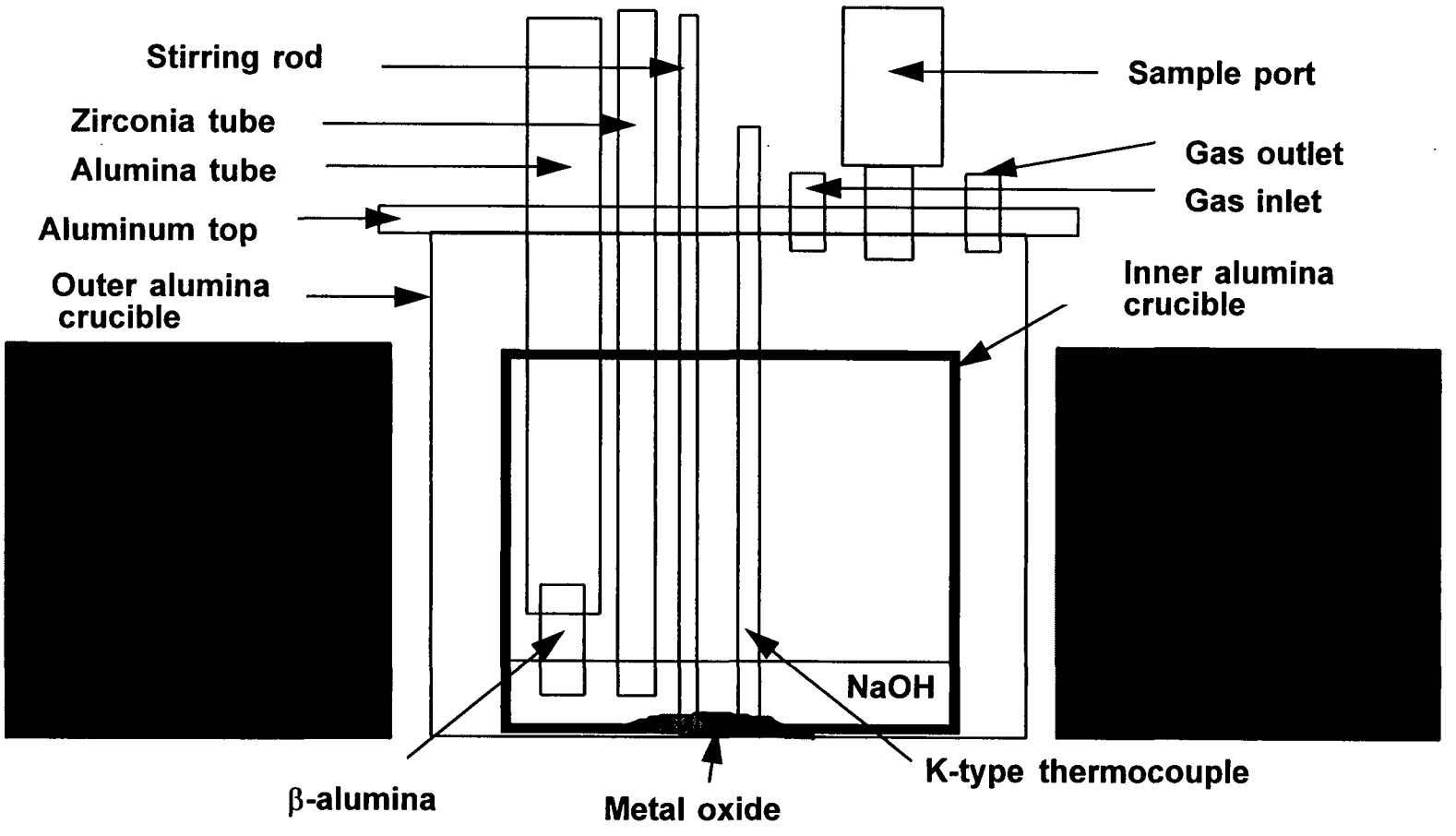
Needs for Hot Corrosion Measurements

- Basicity Measurements
- Basicity Control for Laboratory Tests
- Solubility Measurements to Test Model

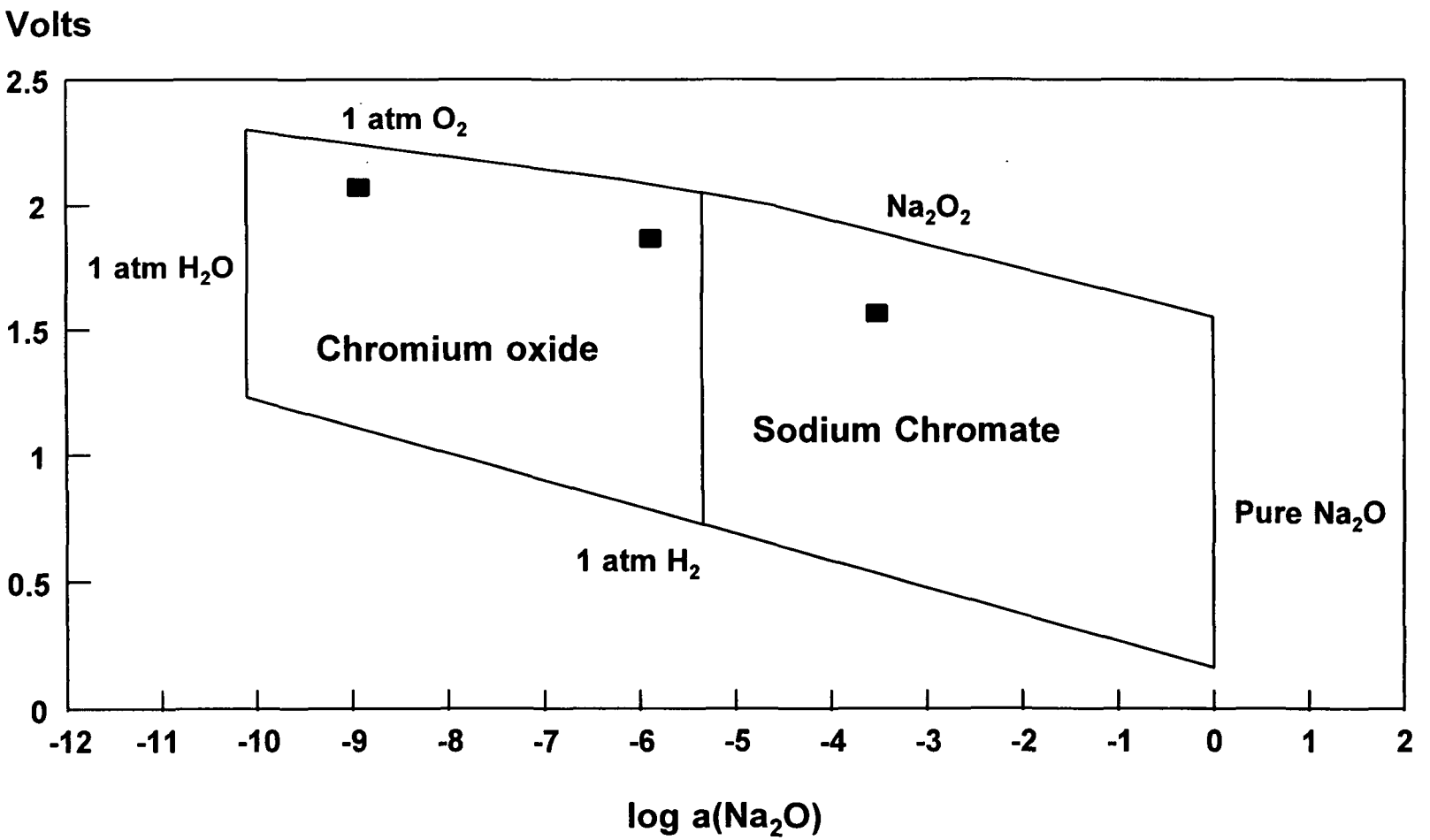
Oxide Solubility Measurements

- Oxide Solubility Minima
  - Acidic vs. Basic Solutes
- Simulate Passive Oxides
  - Pure Oxides of Fe, Cr, Ni
- Effect of Melt Composition
  - KOH Increases Corrosion
  - Temperature Effects
- Goal is to Establish Mitigation Strategies

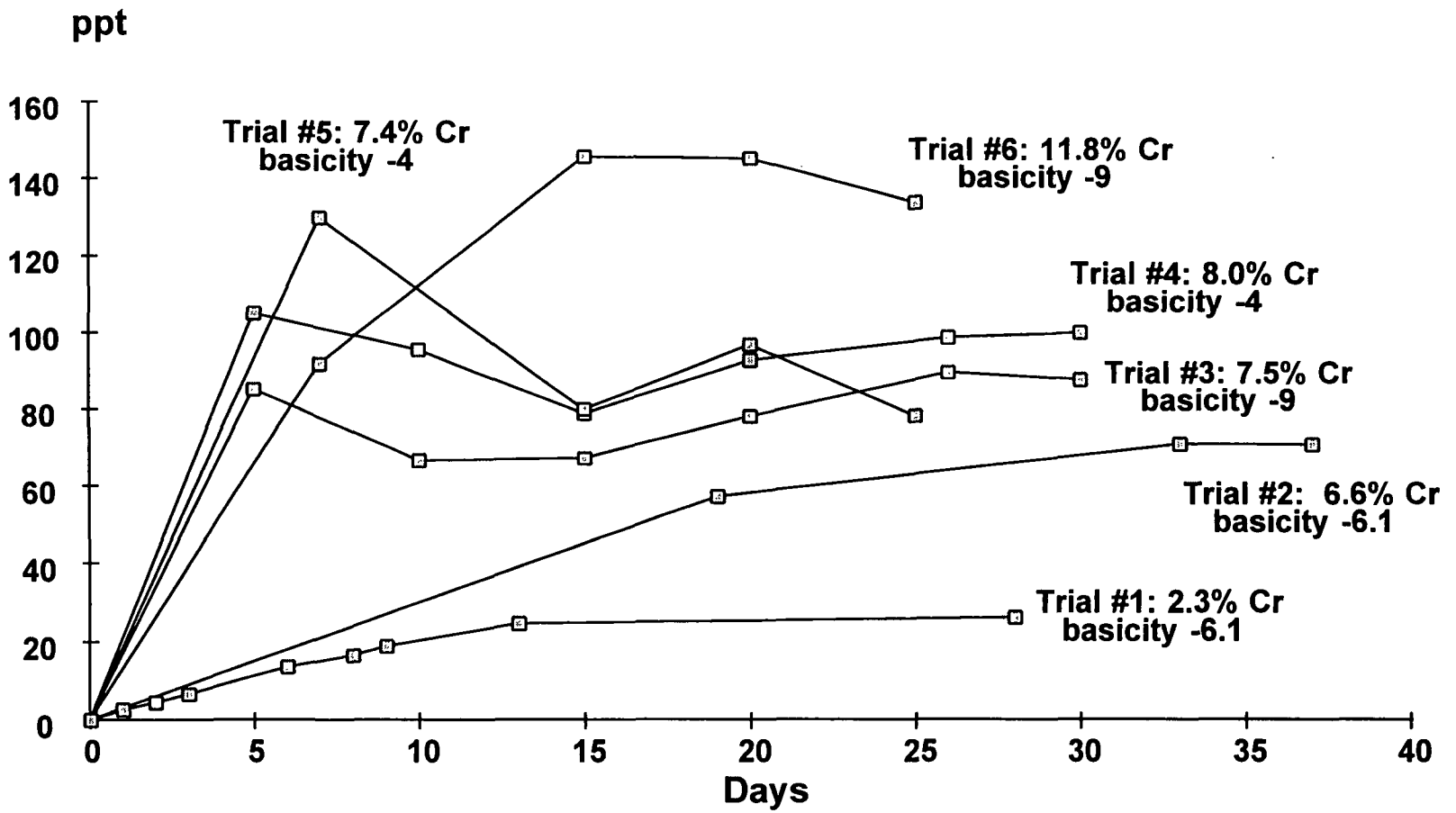
Experimental Setup for Basicity and Solubility Measurements



Phase Stabilities in Na-Cr-O-H System at 350°C



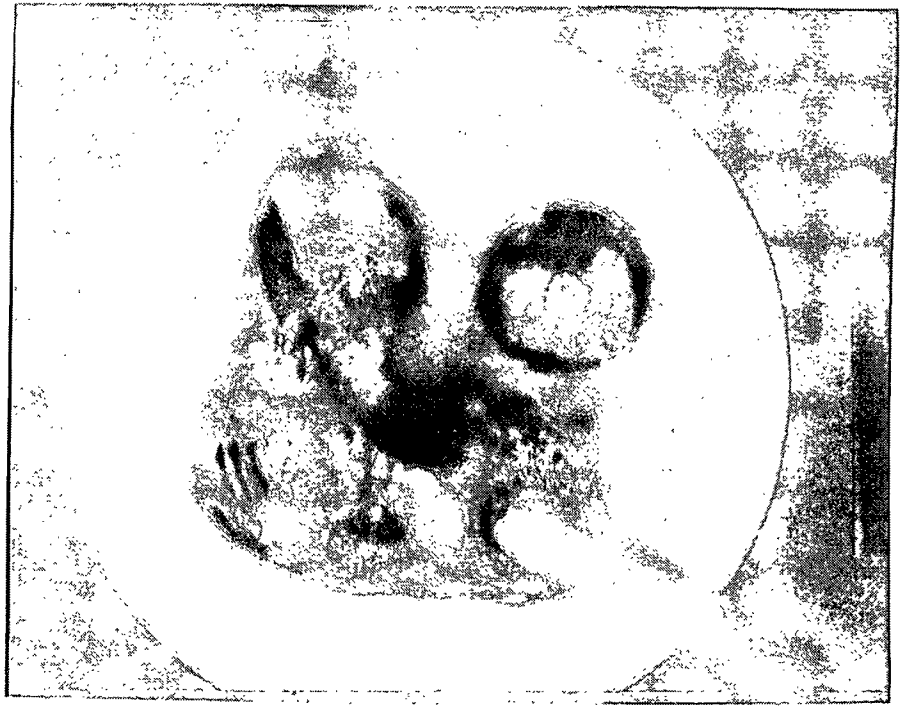
Chromium Content vs. Time for Different Basicities



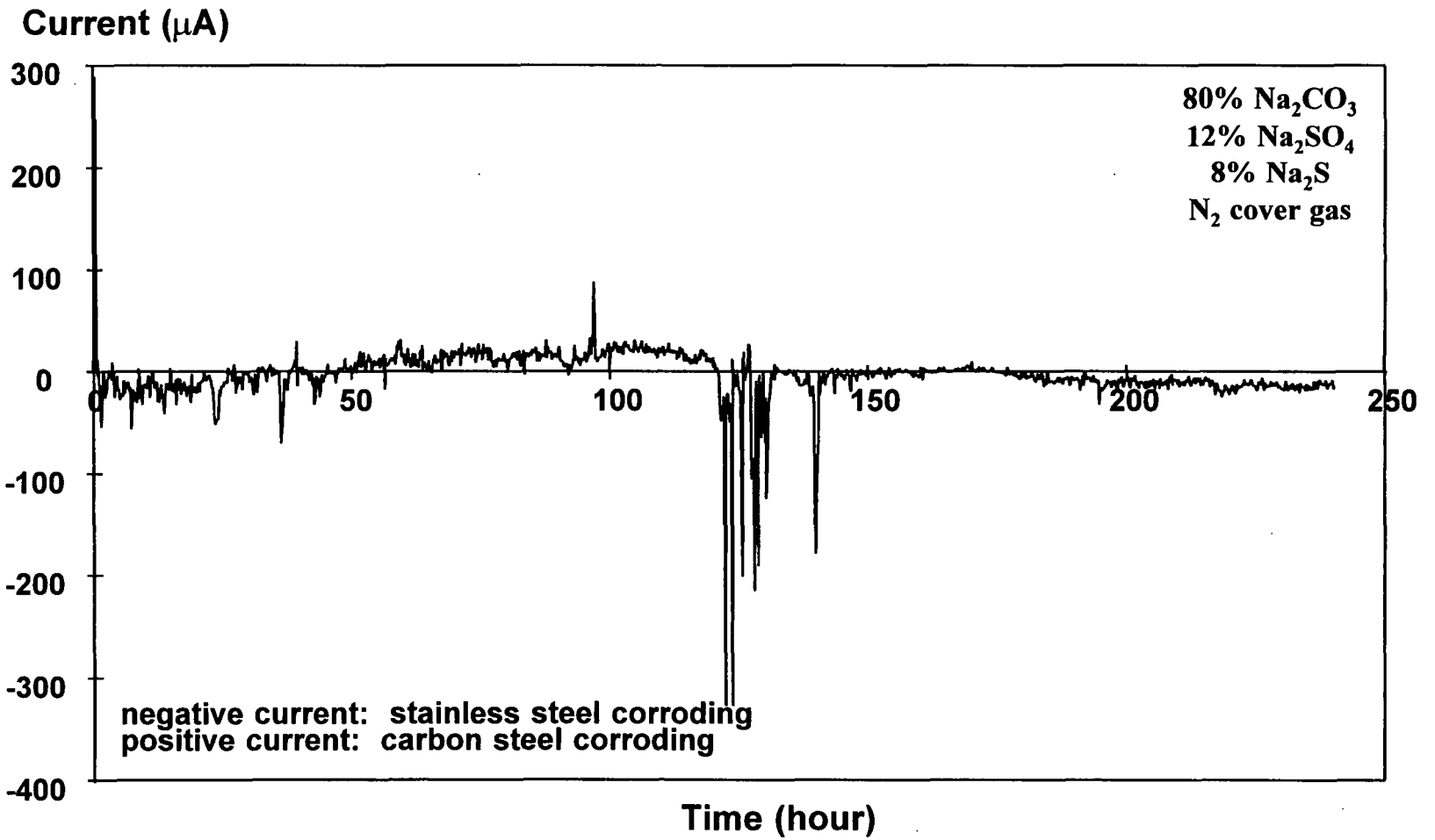
Electrochemical Tests in Molten Smelt

- Question Whether Galvanic Corrosion Plays a Role in Port Corrosion
- Exposed Uncoupled and Coupled 304 Stainless Steel and Carbon Steel
- Measure Current vs. Time

Galvanic Current Probe Electrodes from Molten Smelt Experiment



Galvanic Current between Carbon and Stainless Steels in Molten Smelt at 800°C



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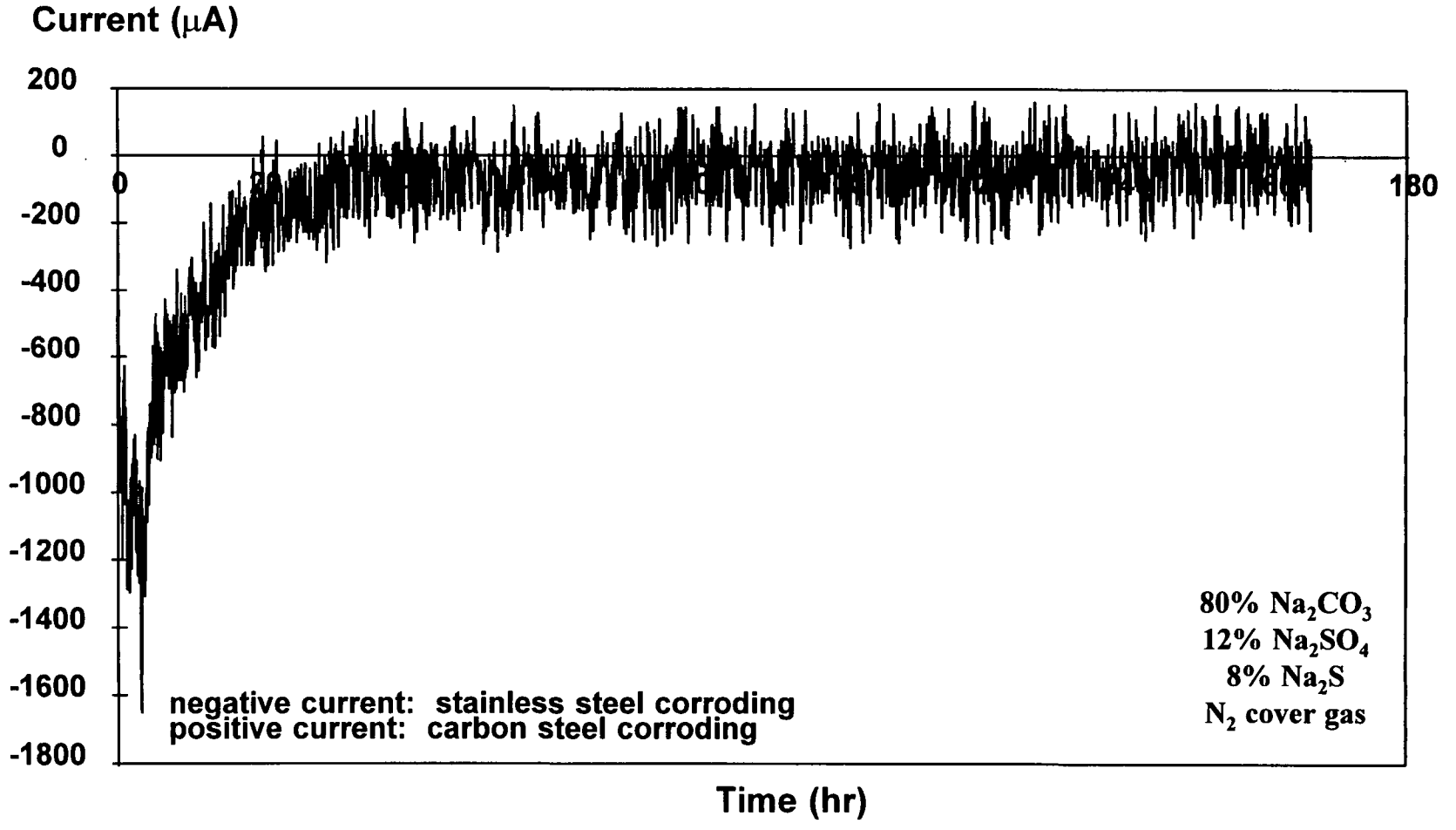

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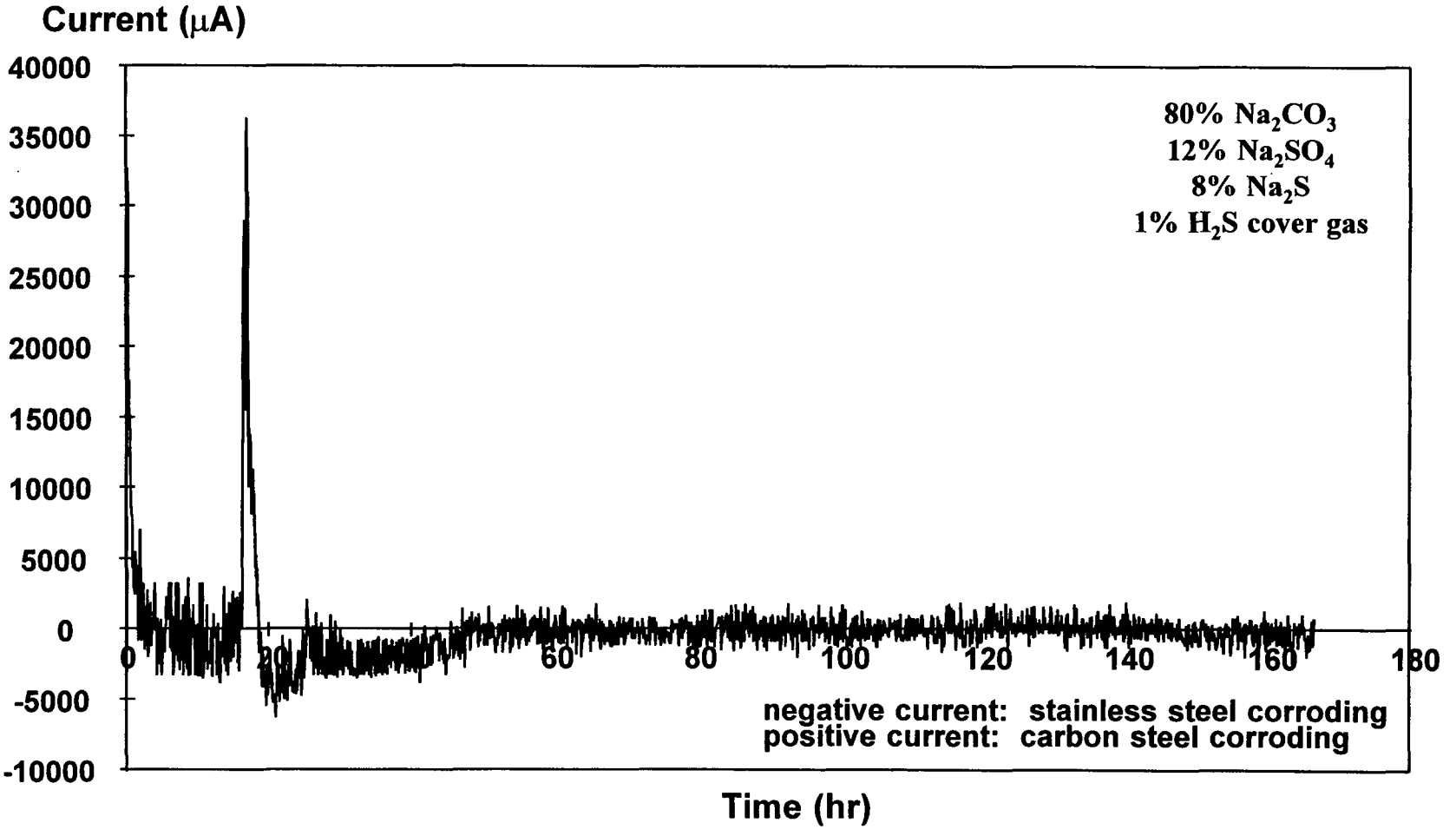
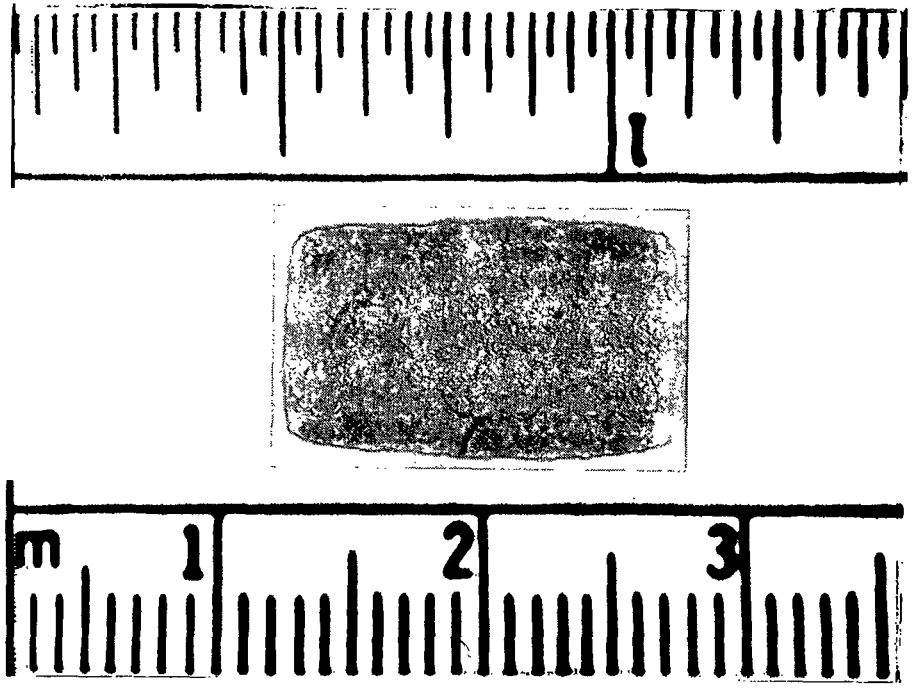
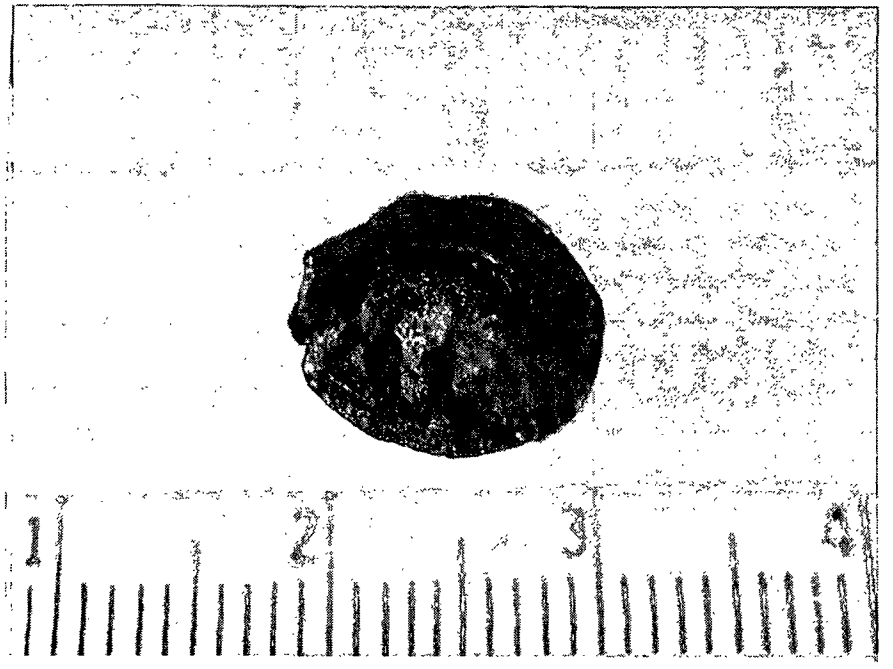


Carbon Steel "Coupon" from Molten Smelt Experiment



Stainless Steel "Coupon" from Molten Smelt Experiment



Conclusions

- At Low SO_2, Cyclic Environmental Changes Also Showed Faster Kinetics
- Scale Analysis Proposal Will be Completed for June Reviews at ORNL
  - scale conversions from sulfide to oxide
- Effect of Alloying Elements Is Currently Under Study

Conclusions (cont.)

- Scaling Kinetics Have Been Determined Using Thermobalance
  - sulfidation: linear
  - oxidation: parabolic
  - alternating: "exponential"
- Port Corrosion Tests Continue as Ph.D. Research
  - Oxide Solubility Curves Being Generated

Conclusions (cont.)

- Molten Smelt Corrosion Tests Completed
  - rates for 304 and carbon steel were thousands of mpy
  - galvanic contribution negligible
  - work fits with externally funded ORNL project

Corrosion Control in Closed-Cycle Mills - F019

- New Project Began July 1
- Objective: identify key corrosion and materials issues which may impact the successful implementation of various closed mill scenarios and provide support to maximize the potential of these new technologies

Milestones

- Fall '94: Complete literature survey on effects of closure relative to environmental effects. Include effort of process scenarios. Develop prioritization scheme.
- Spring '95: Publish materials usability guidelines for different alloys in specific environments

Project Status

- Literature Review Initiated
- Still Needs Work to Complete
  - Some information on process modifications
  - Some materials issues relative to environmental changes
  - There are potentially many ways to reduce mill effluents
  - There are equally many ways to specify materials

Project Status (cont.)

- PAC Discussions
  - Conference Call in December
  - Much Discussion About Priorities
  - Decided to Complete Bleach Plant First
  - Next Will Be the Paper Machine
- EPRI Pulp and Paper Office
  - Time Conflicts Allowed Little Progress
- New Ph.D. Students Will Support Project

Cracking of Composite Tubes in Kraft Recovery Boilers

- Funded by ORNL/DOE; $120K/yr for 4 yrs for IPST, Total Program is $500K/yr
- Year 1 focuses on collecting information about state of understanding
  - failure analyses
  - temperature data
  - site visits; mills and fabricators
- Industrial Advisory Council

Corrosivity Monitoring in Boilers

- Funded By DOE
  - Cost Share of 1/3 by AF&PA
- Will Start at Beginning of Next Fiscal Year
- Total Cost is $1.75 million over 4 years
  - subcontracts to PPRIC, ORNL
- Industry Review Board from AF&PA Recovery Boiler Corrosion Technical Advisory Committee